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STATUS REPORT ON CHEMICAL SYNTHESIS OF
MONOMERIC SELF-SEALANT TYPE ESTERS

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ABSTRACT

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The purpose of this program was to develop an efficient synthetic chemical route for the preparation of alkyl esters of α -cyanosorbic acid (1-cyano-hexadienoic acid) as intermediates in self-sealant polymerization studies. The in-house investigation of the direct and indirect esterification of α -cyanosorbic acid, employing standard and non-conventional techniques, has resulted in the development of a satisfactory procedure for the preparation of n-butyl- α -cyanosorbate and n-amyl- α -cyanosorbate in yields approaching 90 percent. Parallel studies which were initiated by the Research and Technology Division of the Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, (ASD) under Government Work Order H-71461, have resulted in the preparation of n-butyl- α -cyanosorbate in somewhat lower yields with concomitant longer reaction periods. The synthetic procedures developed in both investigations are discussed in detail in this report, and chemical and spectral data are presented to verify the identities of the esters formed in the various reactions.

This program established that the direct esterification of α -cyanosorbic acid is quite feasible and is a much preferred route to the indirect esterification through preparation of such intermediates as the corresponding acid chlorides and sodium salts.

Author

NASA - GEORGE C. MARSHALL SPACE FLIGHT CENTER

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PROPULSION AND VEHICLE ENGINEERING LABORATORY
RESEARCH AND DEVELOPMENT OPERATIONS

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STATUS REPORT ON CHEMICAL SYNTHESIS OF MONOMERIC SELF-SEALANT TYPE ESTERS

SUMMARY

Much interest has developed recently in the chemistry of various alkyl esters of α -cyanosorbic acid because of their potential value as monomers capable of undergoing base catalyzed polymerization to fairly high molecular weight polymers. The physical and chemical properties of these esters make them attractive as candidates for monomers to be utilized as self-sealants in a space environment in which specific components of a vehicle are continually subjected to bombardment by micrometeoroids. The synthesis of these alkyl- α -cyanosorbate derivatives has received little attention until recently.

This report summarizes (1) the status of an internal support program which is directed toward the synthesis of alkyl derivatives of α -cyanosorbic acid and (2) the status of a more concerted parallel effort by the Research and Technology Division of the Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, (ASD) under Government Work Order H-71461.

These two allied programs have demonstrated that various alkyl esters of α -cyanosorbic acid can be prepared very efficiently in a two-step synthetic sequence involving inexpensive and readily available starting materials. Subsequent work by the Air Force has shown that the esters are quite satisfactory for conversion to high molecular weight polymers.

INTRODUCTION

The molecular structure of the esters of α -cyanosorbic acid in which the strongly electronegative nitrile group is attached to the α -carbon atom of a conjugated 1,3-diene system lends itself to the speculation that a base catalyzed addition polymerization reaction of the esters would be quite feasible. Preliminary polymerization experiments employing organic bases such as triethylamine with *n*-butyl- α -cyanosorbate demonstrated that addition polymerization of the monomeric esters can be effected in this manner.

The preparation of alkyl esters of α -cyanosorbic acid has not received particular attention over the past thirty years although a method existed for the preparation of α -cyanosorbic acid (ref. 1).

The acid was not produced commercially until several years ago when the Wyandotte Chemical Corporation prepared sizable quantities under contract to the Aeronautical Systems Division of the Air Force. However, Wyandotte is not making the acid commercially at this time.

In the planned study of the projected synthesis of the alkyl esters of α -cyanosorbic acid, initial emphasis was placed on developing a satisfactory procedure for the preparation of the acid itself. This phase was completed successfully with the synthesis of the acid in high yields based on a modification of the methods reported in the literature (ref. 1 and 2).

The esters of the acid were prepared by a variety of methods; some gave the derivatives in low yield, and others afforded the crude products in near quantitative yield. The methods employed both by Marshall Space Flight Center and by the Air Force under Government Work Order H-71461 are described in detail. Adequate physical and spectral properties are given to support the molecular structures of the synthesized esters.

The author wishes to thank Mr. John Barnes, Mr. Thomas H. Arnold, and Mrs. Sara K. Corbitt of the Chemistry Branch of the Materials Division for the microanalyses and spectral determinations of the synthesized alkyl esters of α -cyanosorbic acid.

STATE-OF-THE-ART

Hamann (ref. 1) reported a method of preparation of α -cyanosorbic acid in 1937 through the base catalyzed aldol-type condensation of crotonaldehyde with sodium cyanoacetate. Later, Andrews et al. (ref. 2) described the preparation of the same acid through a modification of the method of Hamann and also reported the preparation of its ethyl ester. The latter compound was synthesized through the condensation of ethyl cyanoacetate with crotonaldehyde in the presence of piperidine. Andrews reported isolating two isomers of the ethyl ester: a solid, melting point 57-58°C, and a liquid, boiling point 122°C/9 mm.

Earlier, Cawley et al. (ref. 3) reported the preparation of the methyl ester through the reaction of the silver salt of the acid with methyl iodide.

The Wyandotte Chemical Corporation, under the previously mentioned contract with the Air Force, prepared the n-butyl ester of the acid by an undisclosed synthesis. The α -cyanosorbic acid and the n-butyl- α -cyanosorbate then were supplied to the Air Force for study.

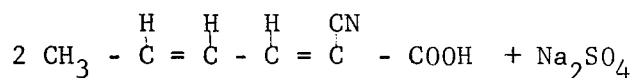
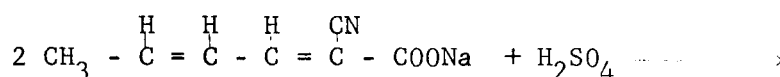
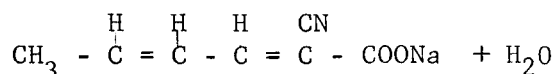
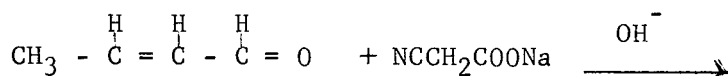
Hamann (ref. 4) studied the base catalyzed polymerization of the alkyl esters of α -cyanosorbic acid and proposed a mechanism of reaction

whereby the strongly electronegative nitrile group on the α -carbon atom gave rise to an inductive effect throughout the length of the conjugated chain which enabled attack by an OH^- on the terminal methyl group with abstraction of one of the protons. It is beyond the scope of this report to elaborate on Hamann's proposed mechanism for the addition polymerization of the esters of α -cyanosorbic acid; reference 4 should be consulted for a detailed account of his studies.

EXPERIMENTAL

Preparation of α -Cyanosorbic Acid

α -Cyanosorbic acid was prepared by a modification of the method of Andrews et al. (ref. 2) through the base catalyzed condensation of crotonaldehyde with the sodium salt of cyanoacetic acid.



A typical preparation is represented by the following procedure: cyanoacetic acid (94.4 g, 1.11 moles) was dissolved in 500 ml of water and cooled with stirring to 10°C . To the stirred solution was added portionwise sodium hydroxide pellets (44 g, 1.11 moles) at such a rate that the temperature of the solution did not exceed 35°C . When all of the sodium hydroxide had been added, any additional base was added to adjust the pH of the solution to 6-7. (It is extremely important that the pH of this solution not exceed 7 at this point.) When the solution was at pH 6-7, the temperature of the solution was lowered to 10°C , and, as stirring was continued, crotonaldehyde (77.8 g, 1.11 moles) was added in one portion. While the resulting two-phase system was maintained at a temperature of 10°C , a dilute aqueous solution (20%) of sodium hydroxide was added dropwise; stirring continued until a pH of 8 was obtained. It was necessary to check the pH of the solution after the addition of every three to four drops to ensure that a pH 8 was not exceeded. When the specified pH was attained, a one-phase system developed with a concomitant yellowish coloration of the solution. Additionally, the temperature of the solution rose to $25\text{-}30^\circ\text{C}$.

The cooling bath was removed from the system at this time, and the stirred solution was allowed to slowly attain room temperature, after which it was stirred overnight. The aqueous solution then was extracted with two 100-ml portions of ether; at this point, no unreacted crotonaldehyde could be detected through its lachrymatory character. The ether extracts were discarded, and the reaction solution was cooled in an ice bath by stirring. To the chilled stirred solution was added 6N sulfuric acid until the mixture was acidic to pH paper; then the solution was allowed to stand at 10-15°C for several hours. Precipitated solid was removed by filtration and washed with ice-cold water (five 100-ml portions). After drying overnight in vacuo over phosphorous pentoxide, the crude α -cyanosorbic acid was recrystallized from an ethanol-water solution (1:4) to give 126.1 g (83%) of long yellowish needles, melting point 169-170°C.

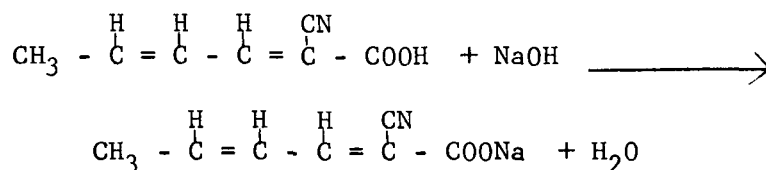
Analysis: Calculated for $C_7H_7NO_2$: C, 61.30; H, 5.15; N, 10.22; N.E., 137.

Found: C, 60.94; H, 5.50; N, 9.95; N.E.; 137.

The infrared spectrum of the acid is illustrated in FIG 1. For comparative purposes, the infrared spectrum of α -cyanosorbic acid synthesized by the Air Force is shown in FIG 2, and the DTA curve of that acid is illustrated in FIG 3.

Preparation of Sodium α -Cyanosorbate

The sodio salt of the acid was prepared through a simple neutralization of the acid in 95 percent ethanol:



The following procedure afforded the salt in near quantitative yield: a solution of sodium hydroxide (8.0 g, 0.2 mole) in 200 ml of 95% ethanol was added in portions to a stirred solution of α -cyanosorbic acid (27.4 g, 0.2 mole) in 200 ml of 95% ethanol. The resulting solution was concentrated in vacuo, and the residual cream-colored solid was dried to constant weight in a vacuum oven at 60°C over phosphorous pentoxide. There were 31.2 g (98%) of the sodium salt obtained which was not further purified or characterized.

Preparation of n-Butyl Chlorosulfite

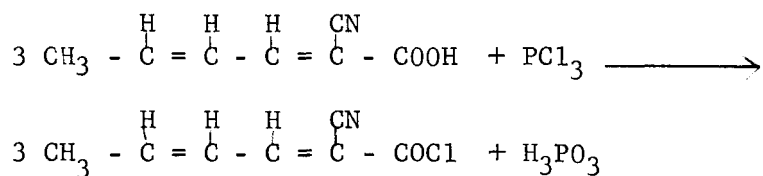
The procedure of Newman and Jones (ref. 5) was used to prepare this alkyl chlorosulfite.



To redistilled thionyl chloride (280 g, 2.34 moles), cooled to 0°C, was added dropwise, with stirring, anhydrous n-butyl alcohol (148 g, 2.0 moles); the temperature was maintained below 15°C. The solution then was allowed to stand at room temperature for 48 hours. The excess thionyl chloride was removed under reduced pressure, and the residue on distillation yielded 295 g (94%) of n-butyl chlorosulfite, boiling point 72-74°C at 28 mm.

Preparation of α -Cyanosorbyl Chloride

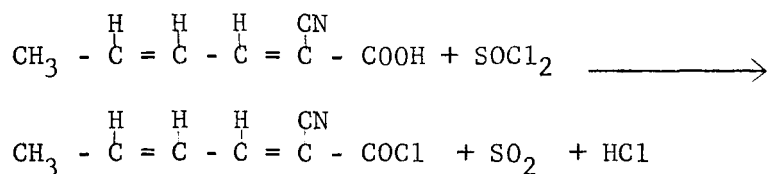
The preparation of the acid halide of α -cyanosorbic acid was accomplished through the use of excess phosphorous trichloride:



α -Cyanosorbic acid (27.4 g, 0.2 mole) was added to 100 ml of phosphorous trichloride, and the mixture was heated to reflux (76°C) for four hours with the system protected from atmospheric moisture. During the heating period, the solid slowly went into solution as the acid chloride was formed. A vigorous evolution of hydrogen chloride occurred throughout the reflux period, presumably because of the reaction of the product, ortho-phosphorous acid, with the excess phosphorous trichloride. After four hours, all solid had gone into solution, and the resulting one-phase system was concentrated in vacuo to remove excess phosphorous trichloride.

The crude acid chloride was obtained as an extremely moisture-sensitive yellow oil. Distillation in vacuo of the crude material afforded 24.9 g (80%) of product as a yellowish oil at 95°-100°C/0.15 mm. Because of the extreme instability of the acid chloride, no attempt was made to obtain elemental analyses or physical or spectral data.

During the Air Force (ref. 6) studies, the α -cyanosorbyl chloride was synthesized in 63 percent yield through the reaction of α -cyanosorbic with thionyl chloride in benzene for two hours at a temperature of 68-70°C.



The acid chloride was obtained as a yellow oil, boiling point 98-100°C/0.1 mm. The elemental analyses and spectral data supported the structure of the compound as being the desired α -cyanosorbyl chloride.

Analysis: Calculated for C_7H_6NOCl : C, 54.03; H, 3.89; N, 9.00; Cl, 22.76.

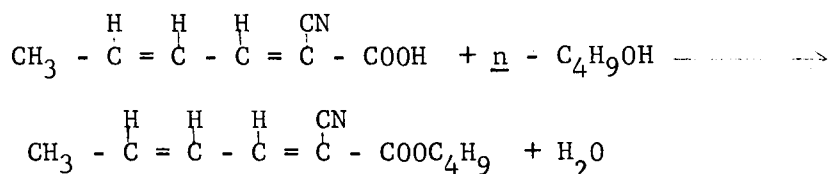
Found: C, 53.76; H, 4.67; N, 9.00, Cl, 22.79.

The infrared spectrum of the acid chloride is illustrated in FIG 4.

Preparation of n-Butyl - α -Cyanosorbate

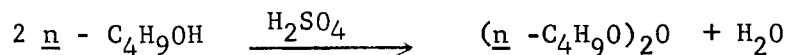
This ester was prepared through several different synthetic techniques. Its synthesis has been described herein because it is a liquid derivative and one of the prime candidates being considered by the Air Force for use in the actual self-sealant system.

The most efficient preparation involved the direct esterification of the acid with n-butyl alcohol in the presence of concentrated sulfuric acid. Additionally, it was found advantageous to add a small amount of hydroquinone to the reaction mixture as an antioxidant. During the course of the study of the esterification reaction, it was found that the concentration of the acid with respect to the alcohol was quite critical. At an acid concentration of 15 percent in the n-butyl alcohol (w/w), the reaction went to completion in approximately two hours, as evidenced through the azeotropic separation of the water formed in the reaction:



At lower acid concentrations (5-10%), the evolution of the water of reaction was considerably slower and, in most instances, ceased after only 50 percent of the theoretical volume of water had been collected.

At this fairly high level of acid concentration, the competing side reaction of the bimolecular dehydration of the alcohol itself to the corresponding ether had to be considered:



It was established that under the conditions employed for the esterification of the acid described below no dehydration of the alcohol occurred when the reaction was run without the presence of the

α -cyanosorbic acid. The fact that no water of reaction was azeotropically collected from the refluxing n-butanol-sulfuric acid system proved that no reaction was occurring. As will be described later, this was found not to be the situation when the esterification was effected with n-amyl alcohol.

In a typical experiment, α -cyanosorbic acid was added to 100 ml of anhydrous n-butanol containing 0.2 g of hydroquinone. To the stirred mixture, 8 ml of concentrated sulfuric acid were slowly added. The flask then was connected to a Dean-Stark water trap, which was connected to a Friedrich condenser. The stirred mixture was slowly heated to reflux and maintained at this temperature for two hours; during this time, 3.8 ml of water collected in the Dean-Stark trap. The cooled solution was poured into 500 ml of water; the organic layer was separated, washed with water until the washings were neutral to pH paper, and then dried over anhydrous magnesium sulfate overnight.

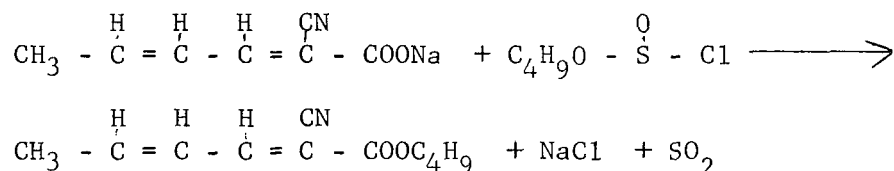
The mixture was filtered; the filter cake was washed with anhydrous ether; and the combined filtrate and washings were concentrated in vacuo to give 36.3 g (94%) of crude product like a brown oil. Vacuum distillation of the residue at 101-105°C/0.3 mm afforded 31.7 g (82%) of the n-butyl ester as a pale yellow oil.

Analysis: Calculated for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25

Found: C, 67.44; H, 7.74; N, 7.01.

The infrared spectrum of the ester is illustrated in FIG 5.

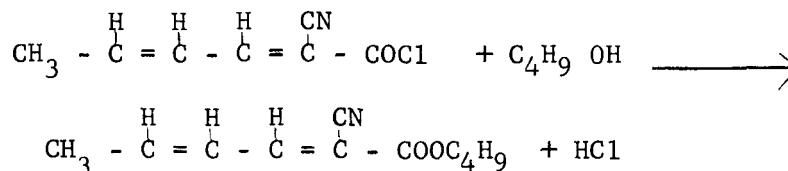
A second, much less productive method involved the reaction of the sodium salt of the α -cyanosorbic acid with n-butyl chlorosulfite in an adaptation of Newman's method (ref. 5) for the preparation of butyl esters.



In a typical run, n-butyl chlorosulfite (30 g, 0.19 mole) was added to a mixture of sodium- α -cyanosorbate (15.9 g, 0.1 mole) in 100 ml of dry chlorobenzene. The stirred mixture was heated slowly to 110°C; at which time a steady evolution of sulfur dioxide began. At the end of 1.5 hours, the evolution of gas had essentially ceased, and the cooled reaction mixture was poured into 100 ml of water. The emulsified system was filtered to give 8.2 g of regenerated α -cyanosorbic acid, melting point 169-172°C. The two-phase filtrate was separated. The organic layer was dried over anhydrous magnesium sulfate and then filtered.

The filtrate was concentrated in vacuo, and the residue was vacuum distilled at 100-101°C/0.3 mm to give 7.0 g (36%) of the ester as a pale yellow oil.

The third method to be evaluated involved the reaction of the α -cyanosorbyl chloride with n-butyl alcohol:



In this reaction, α -cyanosorbyl chloride (30.2 g, 0.19 mole) was added dropwise to 250 ml of refluxing n-butyl alcohol at a rate so as to maintain a steady evolution of hydrogen chloride. The solution was heated for one hour after the evolution of the gas had ceased. The solution was concentrated under reduced pressure and the residue distilled in vacuo at 100-105°C/0.3 mm to give 33.1 g (85%) of the butyl ester as a yellow oil.

During the studies, the Air Force (ref. 6) investigated several methods for the preparation of the butyl ester of α -cyanosorbic acid. The most productive synthesis involved the direct esterification of the acid with n-butanol in the presence of anhydrous hydrogen chloride.

In a typical run, n-butanol (2060 g, 15.04 moles) was cooled to 2-4°C and saturated with anhydrous hydrogen chloride. To this solution was added α -cyanosorbic acid (500 g, 3.65 moles). The solution was heated to reflux (92°C) and the butanol-water azeotrope allowed to distill from the reaction system. When no more water was azeotropically collected, the reaction solution was chilled to 2-4°C and re-saturated with anhydrous hydrogen chloride. The solution was then heated to reflux, and additional water of reaction was allowed to distill from the system. This process was repeated over a three to four-day period until no more water of reaction could be azeotropically removed from the system.

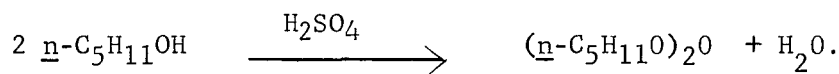
At this point, the excess alcohol was removed by distillation and the residue distilled at 98-99°C/0.1 mm to yield 584.1 g (83%) of ester.

The infrared spectrum of the Air Force ester is illustrated in FIG 6.

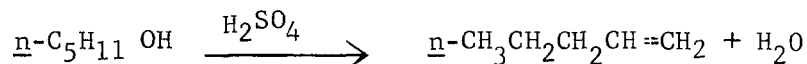
In a similar fashion, the following esters of α -cyanosorbic acid were prepared in the specified yields: methyl- α -cyanosorbate (45%); ethyl- α -cyanosorbate (26%); n-octyl- α -cyanosorbate (56%); n-cetyl- α -cyanosorbate (73% crude). When catalytic amounts of p-toluene sulfonic acid were used in one experiment, n-amyl- α -cyanosorbate was obtained in 29% yield.

Preparation of n-Amyl- α -Cyanosorbate

This ester was prepared in a manner similar to that described earlier for the preparation of n-butyl- α -cyanosorbate. In studying the esterification with n-amyl alcohol, it was found that, at the sulfuric acid concentration employed, bimolecular dehydration of the alcohol could take place with the formation of di-n-amyl ether:



To a much lesser extent, it was observed through gaseous evolution from the condenser that monomolecular dehydration of the alcohol was occurring with the formation of the olefinic amylene:



That these two competing side reactions were occurring was established by allowing a solution of the acidified n-amyl alcohol to reflux while connected to a Dean-Stark water trap. After a short induction period, the water of reaction started azeotropically distilling into the trap (90%). When no more water could be collected, the reaction solution was washed to neutrality with water and dried over anhydrous magnesium sulfate; the solid was removed by filtration, and the filtrate was fractionated. Initially, unreacted n-amyl alcohol, boiling point 138-139°C, was collected followed by the di-n-amyl ether, which distilled at 182-185°C in 70% yield, literature boiling point 184-186°C (ref. 7).

In the esterification with n-amyl alcohol, it was necessary to discontinue the reaction when the theoretical volume of water of reaction had been collected. However, if the theoretical volume of water was exceeded, no harm was done because the boiling point of the di-n-amyl ether is considerably below the boiling point of the n-amyl- α -cyanosorbate and can be collected in the forerun when the crude ester is fractionally distilled. The acid preferentially esterifies before dehydration of the alcohol begins.

The following procedure describes the preparation of the n-amyl ester: α -cyanosorbic acid (27.4 g, 0.2 mole) was added to 250 ml of anhydrous n-amyl alcohol which contained 2 g of hydroquinone. To the stirred mixture was slowly added 20 ml of concentrated sulfuric acid. The flask then was connected to a Dean-Stark water trap, which was in turn connected to a Friedrich condenser. The stirred mixture was heated slowly to reflux and maintained at this temperature for 0.5 hour, at which time the theoretical volume (3.6 ml) of water of reaction had been collected. The reaction solution was worked as described in the preparation of n-butyl- α -cyanosorbate to give 43.8 g (95%) of product. The

crude ester was fractionally distilled in vacuo, and the ester was collected at boiling point 111-116°C/0.25 mm . There were 36.4 g (88%) of ester obtained as a pale yellow oil.

Analysis: Calculated for $C_{12}H_{17}NO_2$: C, 69.53; H, 8.27; N, 6.76.

Found: C, 68.01; H, 8.02; N, 7.01.

The infrared spectrum of the ester is illustrated in FIG 7. For comparative purposes, the infrared spectrum of the ester prepared by the Air Force is illustrated in FIG 8.

CONCLUSIONS

The two areas of investigation described herein have independently established efficient and practical synthetic methods for the preparation of alkyl esters of α -cyanosorbic acid for ultimate application in space-oriented programs as self-sealants.

The method developed by the Air Force is somewhat more time-consuming than the method developed at MSFC; nevertheless, it accomplishes the same goal in somewhat lower yields.

Because of the fairly high degree of success in synthesizing these esters, additional effort should not be expended in this area of research, but, rather, efforts should be directed toward the actual polymerization of the esters to high molecular weight polymers suitable for functioning as self-sealants in a space environment.

To this end, various organic bases will have to be evaluated as catalysts for the addition polymerization reaction. Also, a detailed study should be made of the effect of temperature on the rate of the polymerization reactions. It is hoped that the results of this several-phase study will provide an acceptable self-sealant system capable of functioning in its intended environment.

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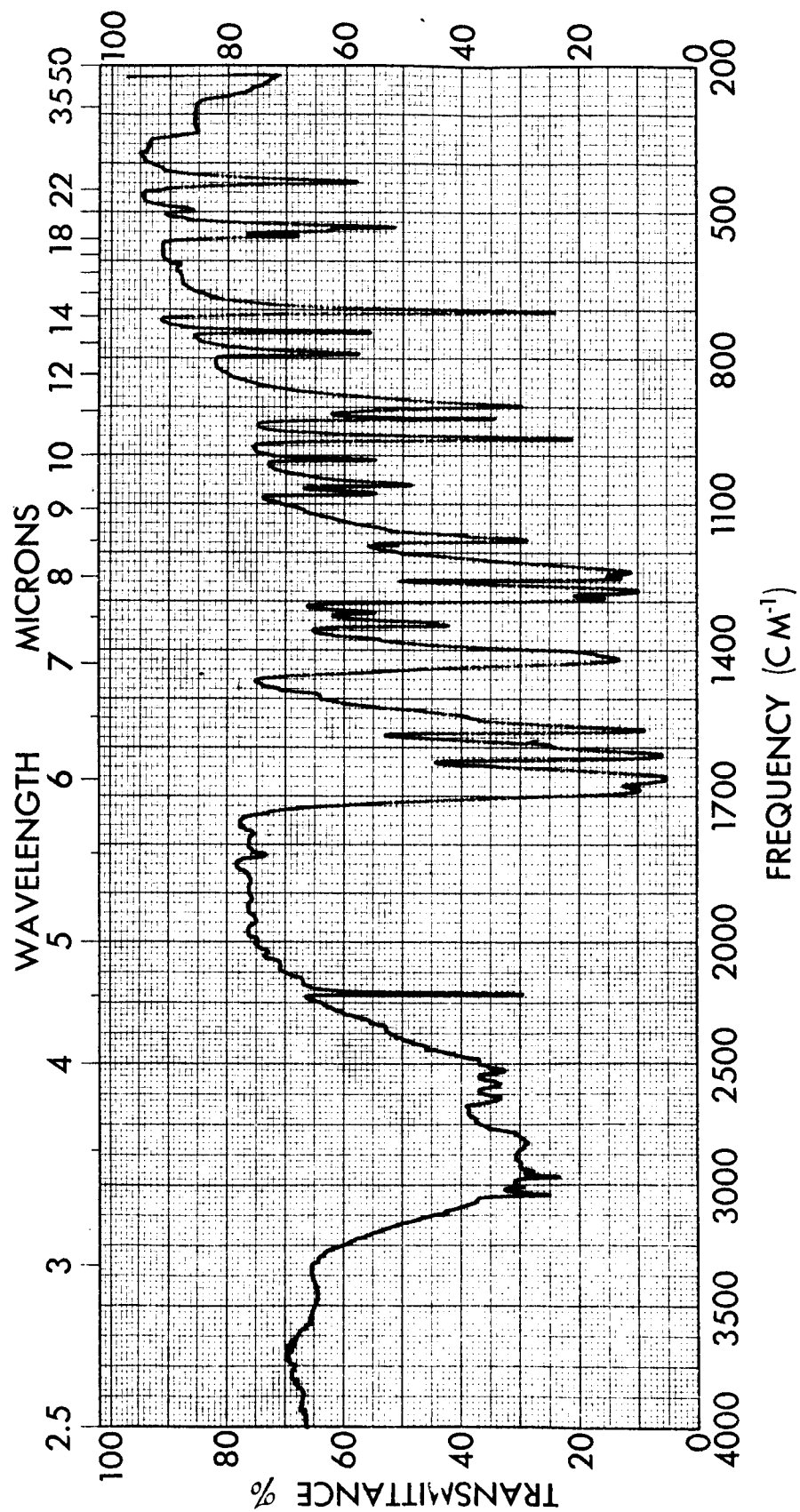


FIGURE 1. INFRARED SPECTRUM OF α -CYANOSORBIC ACID (MSFC)

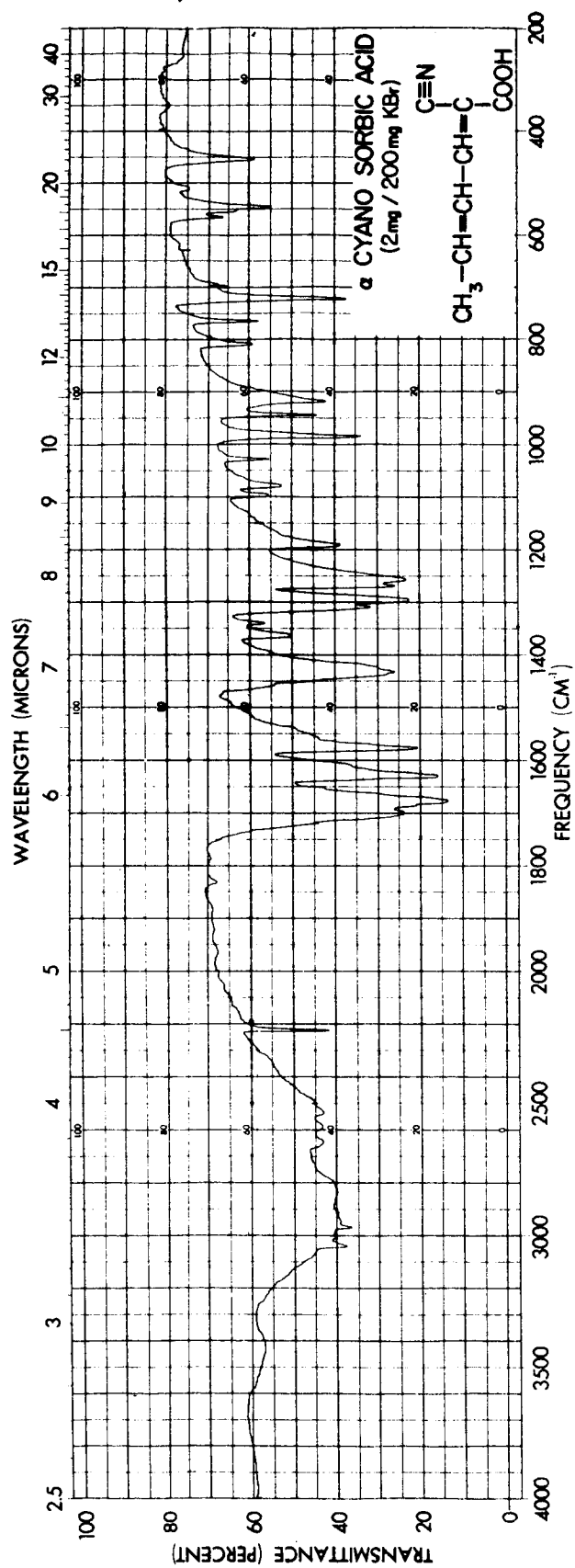


FIGURE 2. INFRARED SPECTRUM OF α -CYANOSORBIC ACID (ASD)

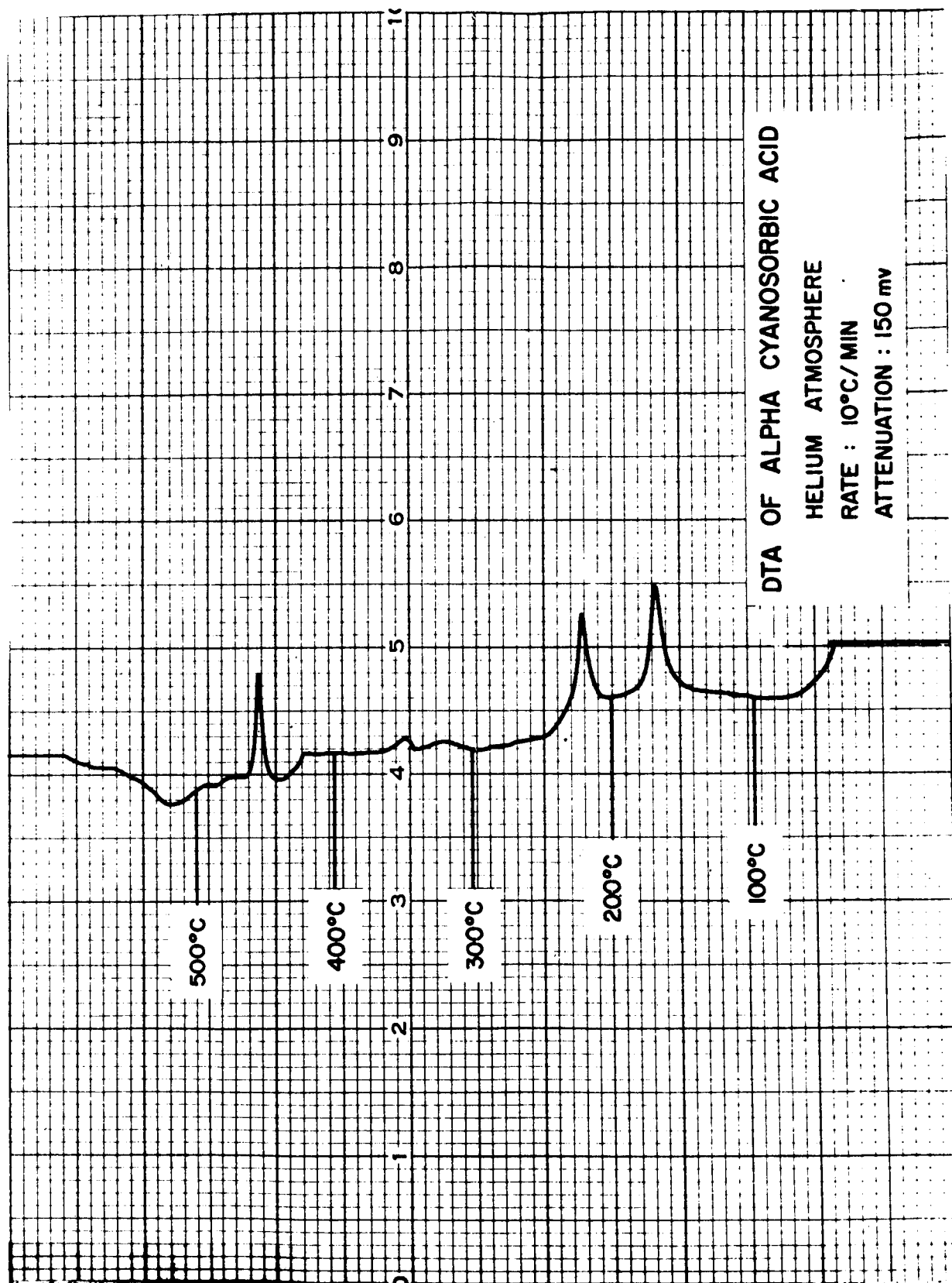


FIGURE 3. DIFFERENTIAL THERMAL ANALYSIS OF α -CYANOSORBIC ACID (ASD)

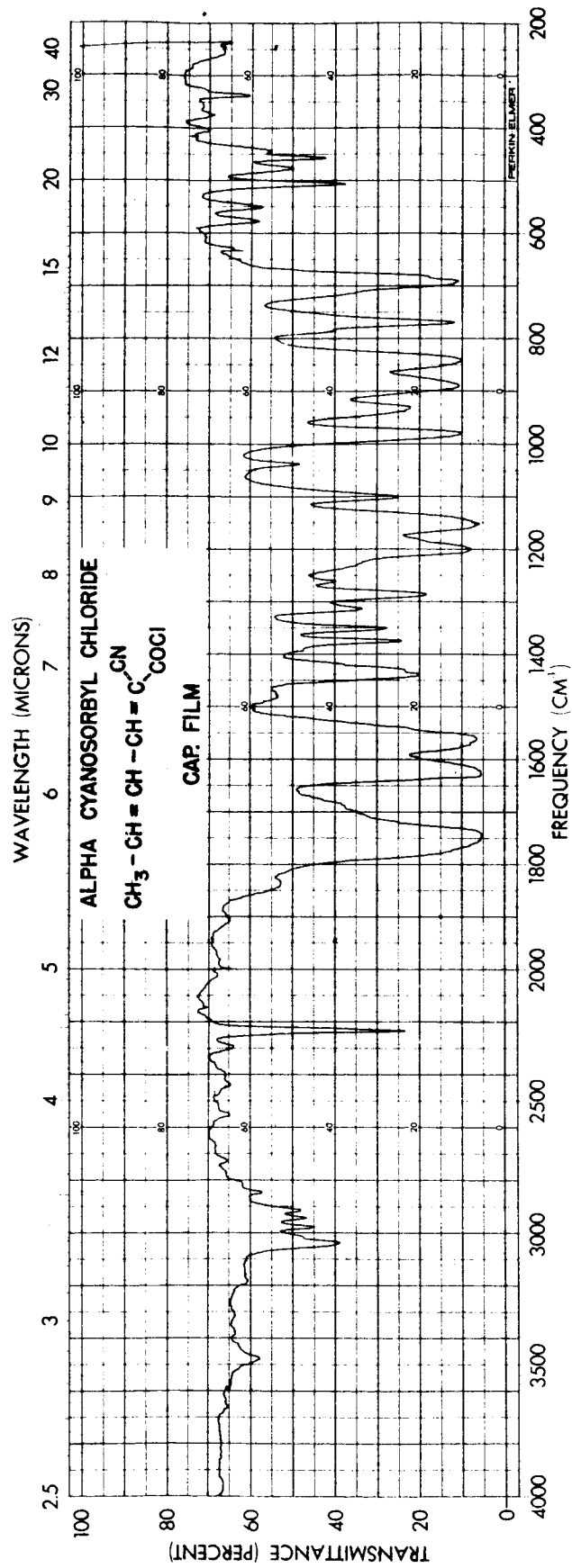


FIGURE 4. INFRARED SPECTRUM OF α -CYANOSORBYL CHLORIDE (ASD)

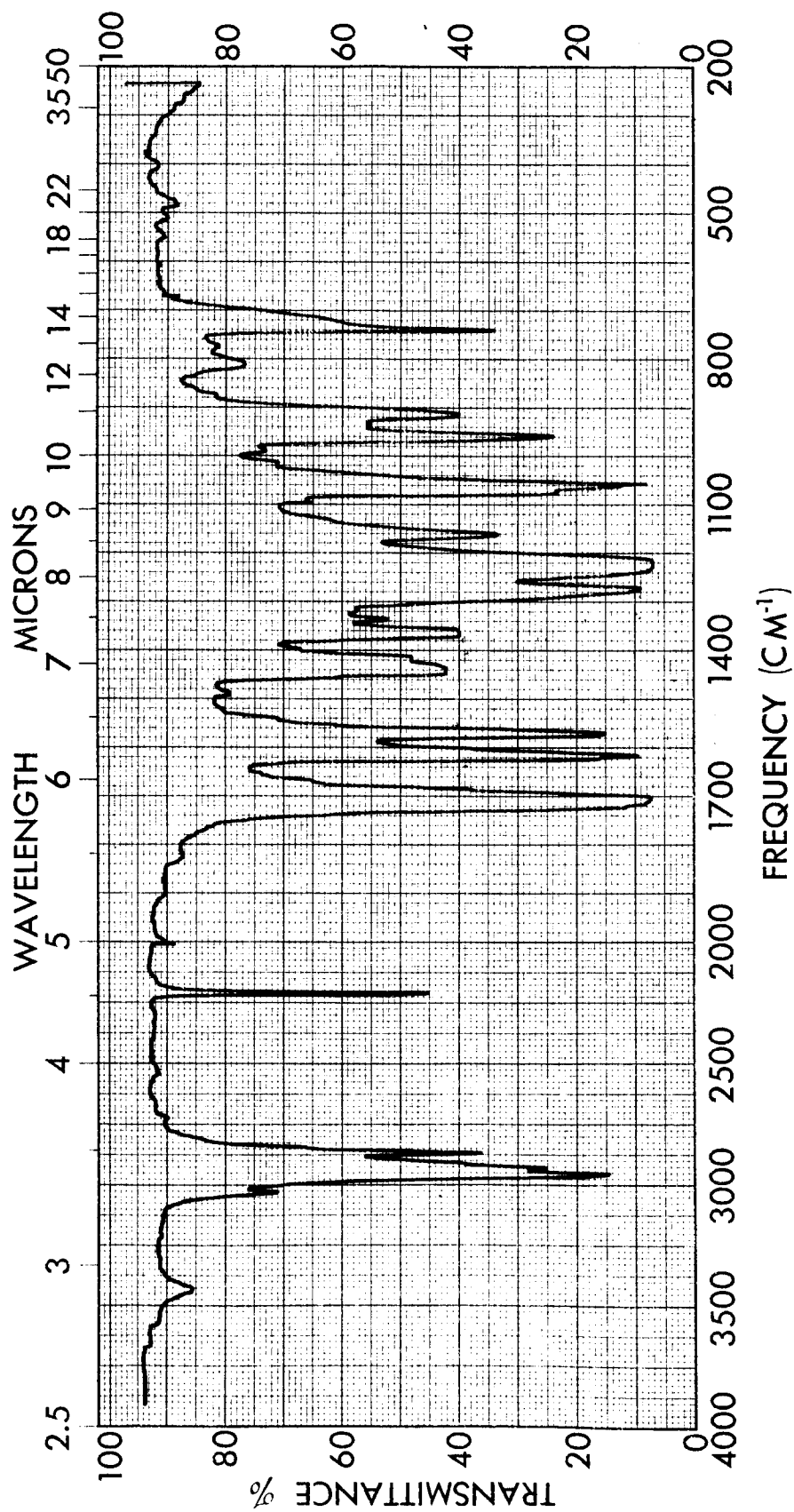


FIGURE 5. INFRARED SPECTRUM OF *n*-BUTYL- α -CYANOSORBATE (MSFC)

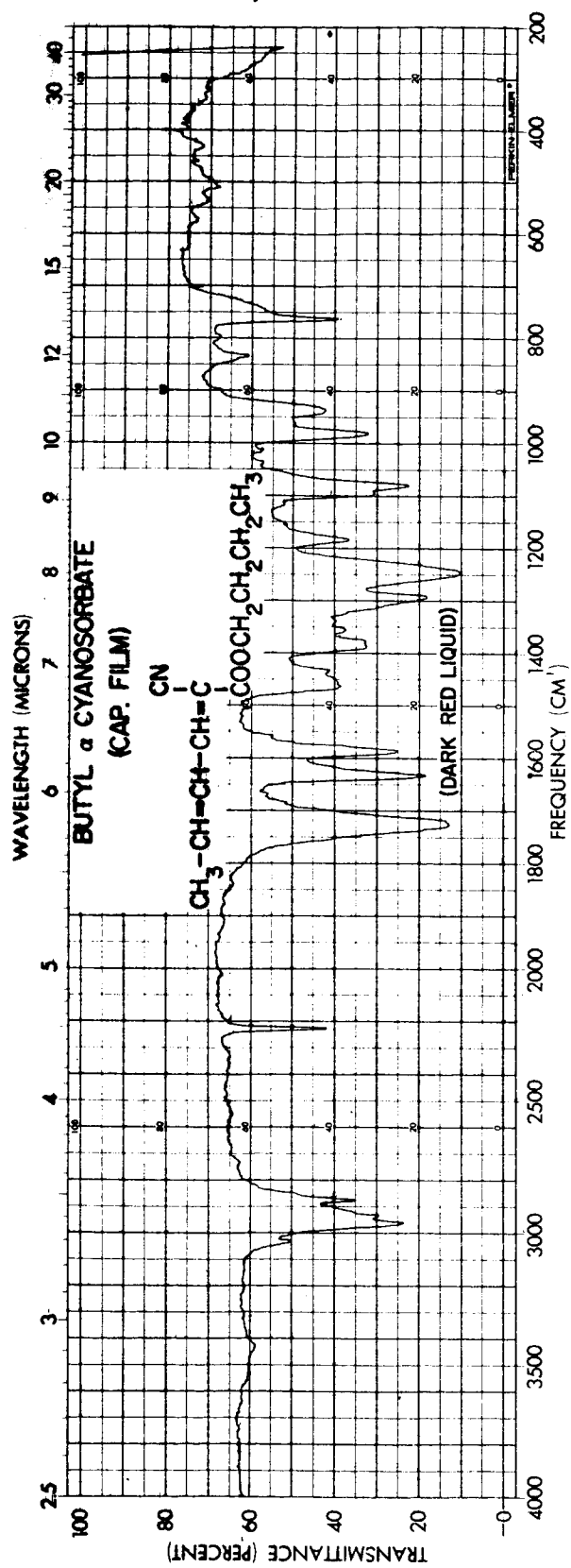


FIGURE 6. INFRARED SPECTRUM OF α -BUTYL- α -CYANOSORBATE (ASD)

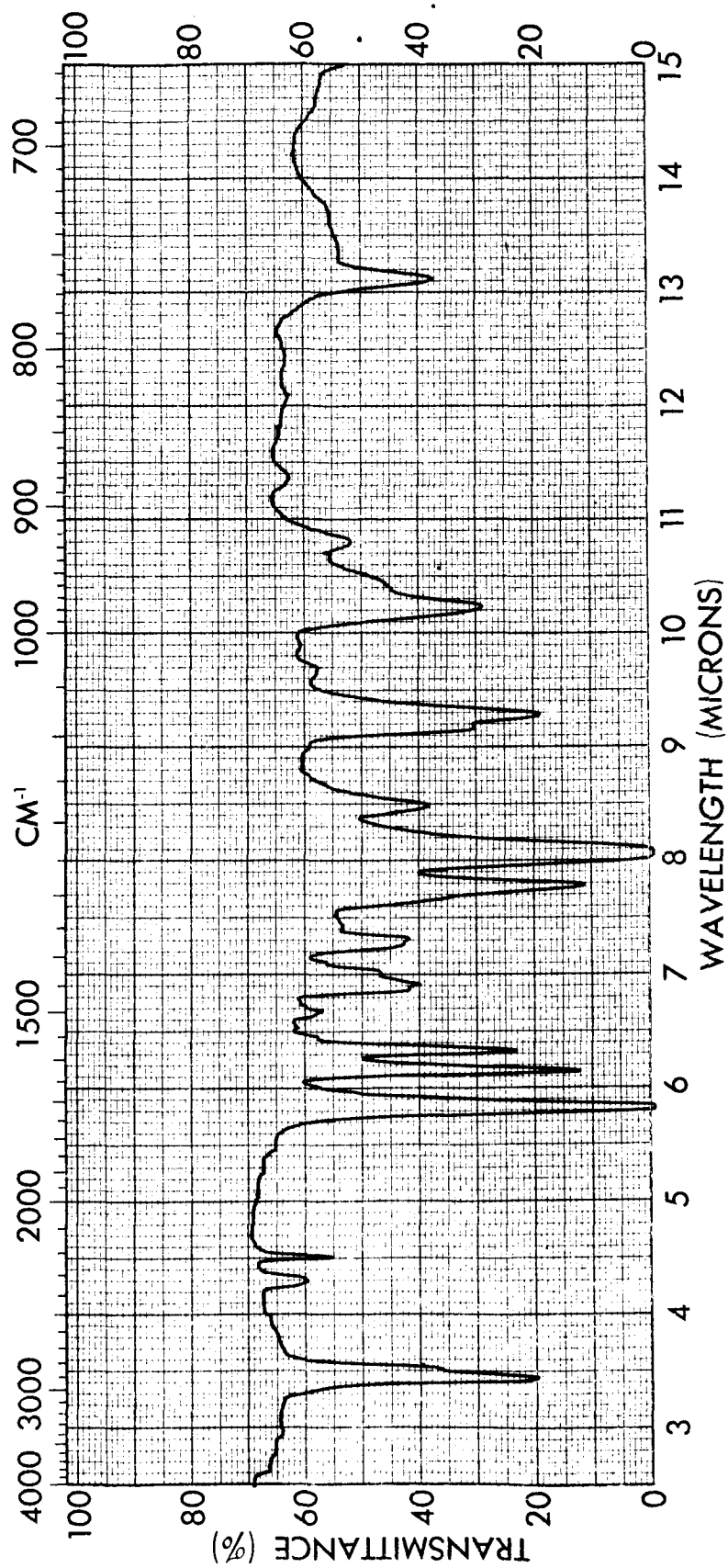


FIGURE 7. INFRARED SPECTRUM OF n-AMYL-O-CYANOSORBATE (MSFC)

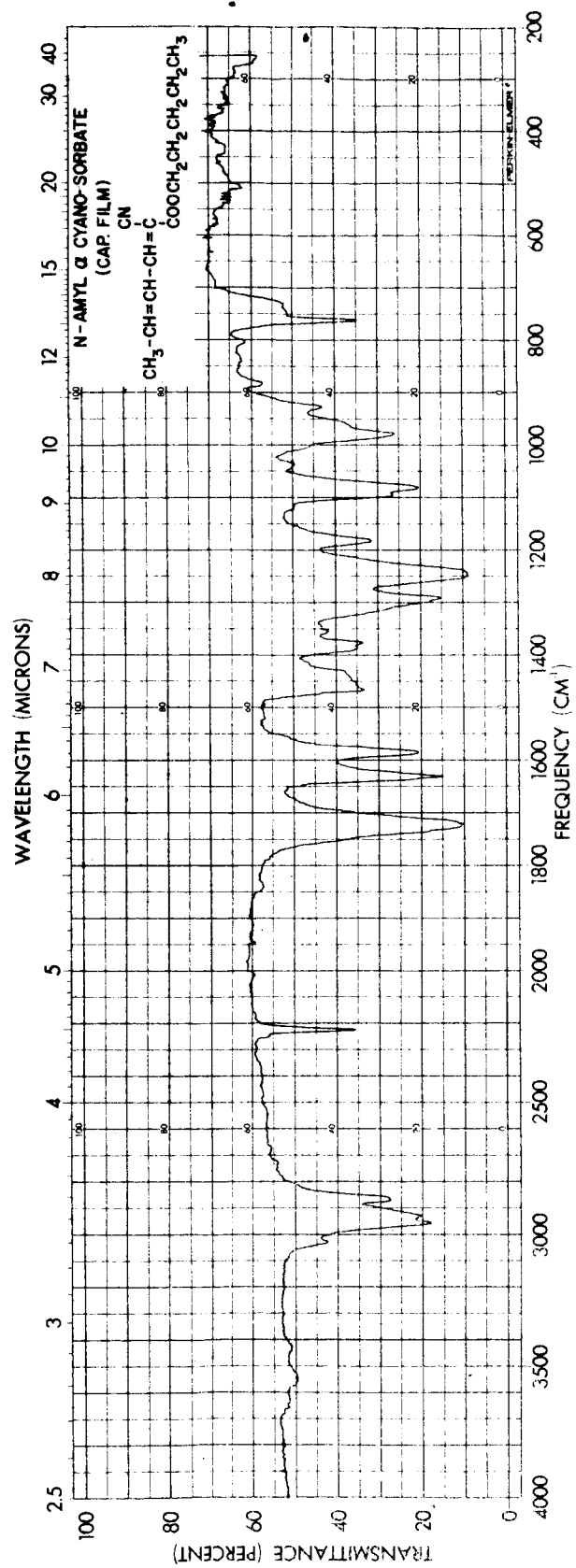


FIGURE 8. INFRARED SPECTRUM OF n-AMYL-α-CYANOSORBATE (ASD)

November 4, 1965

APPROVAL

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STATUS REPORT ON CHEMICAL SYNTHESIS OF MONOMERIC
SELF-SEALANT TYPE ESTERS

By Lawrence R. Moffett, Jr.

The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

This document has also been reviewed and approved for technical accuracy.



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